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COLORED AND COATED PLATE-LIKE PIGMENTS

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COLORED AND COATED PLATE-LIKE PIGMENTS

[Gefärbte und Beschichtete Plättchenförmige Pigmente]

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The invention concerns lamellar pigments with high gloss and high covering power or high transparency.

Frequently, covering power and gloss can be realized at the same time to a satisfactory extent only with difficulty in the case of lamellar pigments. For instance, mica flakes coated with one or more thin metal oxide layers are characterized by interference colors and high gloss, but, because of the transparent substrate, also by high transparency and thus comparably low covering power. The covering power can be improved by using colored metal oxide layers of chromium oxide or iron oxide, for example, but the covering power of such pigments frequently does not satisfy all requirements. The covering power can be increased further if the substrate surface is rough, or if relatively rough metal oxide layers are deposited: the covering power increases because of the increased number of scattering centers, but the gloss diminishes.

The thickness of the metal oxide layers is typically between 50 and 250 nm, in each case according to the refractive index of the metal oxide that is used and the desired interference color. Since reflections occur at the phase boundary of materials with different optical refractive indices, interference effects are observed in reflected light when the lamellar pigments are aligned in parallel, with these effects being dependent on the observation angle and the optical thicknesses of the metal oxide layers; In transmitted light, one sees the corresponding complementary color in the case of nonabsorbing materials.

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A smooth substrate surface is a prerequisite for the realization of such interference effects.

Up to now, chiefly natural materials such as mica have been used as lamellar substrates for the manufacture of interference pigments. Since they are naturally occurring materials, the surfaces of such substrates are not ideally smooth, but rather they have irregularities such as ledges, for example, so that the quality of the resulting interference pigment is limited.

Another drawback to natural materials such as mica are contaminations by color-producing foreign ions, for example iron ions, which can have an adverse effect on the color uniformity of the end product.

It has further been proposed that lamellar metal substrates be used instead of transparent mica, which leads to pigments with very high covering power. On the other hand, a very hard, metallic gloss results at the same time, which frequently is not aesthetically completely satisfactory. In addition, metal pigments do not have any effect of depth, since the incident light is immediately reflected from the surface.

* Numbers in the right margin indicate pagination in the original foreign text.

Thin glass flakes that are obtained by rolling a glass melt and then grinding it have been proposed as a synthetic material. Interference pigments based on such materials do have color effects that are superior to the traditional mica-based pigments. However, it is drawback that the glass flakes have a very high average thickness of about 10-15 μm and a very broad distribution of thicknesses (typically between 4 and 20 μm), while the thickness of interference pigments is typically no greater than 3 μm . EP 0,384,596 describes a method in which hydrated alkali silicate is bubbled with an air jet at temperatures of 480-500°C, forming bubbles with thin walls; the bubbles are then broken up to produce lamellar alkali silicate substrates with a thickness of less than 3 μm . However, the process is costly and the thickness distribution of the resulting flakes is relatively broad.

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EP 0,240,952 proposes a continuous conveyor belt method for producing various lamellar materials, including silicon dioxide. Here a thin liquid film of a precursor of the lamellar material with a specific thickness is applied to a smooth conveyor belt via a roller system; the film is dried and separated from the conveyor belt, whereupon lamellar particles are formed. The particles are then optionally annealed, optionally ground and classified.

Organometal compounds (alcoholates) such as tetraethyl orthosilicate are used as precursor materials. The film is polymerized by drying and scraped from the belt by means of a doctor scraper, with small flakes being obtained; for conversion to the corresponding metal oxide, these flakes are then annealed at temperatures of 500°C. In addition, a metal oxide sol optionally dispersed in methanol is used as a precursor, which is similarly applied as a film, dried and annealed.

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However, the use of very costly precursor materials and, in particular, the higher requirements on workplace safety that have to be in place when using organometal compounds are drawbacks. The complete chemical conversion of the precursor to the desired layer material, as a rule, makes significant heating of the film and the conveyor belt material necessary. Besides the considerable thermal stress on the conveyor belt material that occurs, the high energy costs and limitation of process speed have very disadvantageous effects on the economy of the process.

Also, the use of aqueous oxide or hydroxide sols described in EP 0,236,952 is problematic, since the resulting films are not homogeneous, but rather are formed of particles of uneven size. This necessitates a treatment at very high temperatures in order to give the material the necessary homogeneity, precision of shape and durability.

US 3 138 475 describes a continuous conveyor belt method for producing lamellar or tinsel-like oxides or oxide hydrates of metals of groups IV and V and the iron group of the periodic system. Here a parting layer of, for example, silicone paint is first applied to a circulating conveyor belt in order to facilitate subsequent detachment of the metal oxide layer.

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Then a liquid film of a solution of a hydrolyzable compound of the metal that is to be converted to the desired oxide is applied, the film is dried and then detached with the aid of a vibrating device. It is noted that SiO_2 flakes can also be produced by this method, but the method is really only generally described and no specific example is given.

JP 64-9803 describes a method for producing a lamellar metal oxide with dispersed fine particles of a second metal oxide that has a higher refractive index, on an endless conveyor belt. The products obtained by this method, which are used as sunscreen filters in cosmetics, for example, consist of a matrix of silicon dioxide in which fine particles of titanium dioxide are dispersed. However, this product does not show any interference colors, since the titanium dioxide particles that act as scattering centers are not uniformly distributed on a smooth surface.

A pigment is known from JP 2-32 170 that consists of a base material, for example, a titanium dioxide-mica pigment, where colloidal metal particles (silver) are sputtered onto a first interference layer of titanium dioxide. Then, as before, titanium dioxide is applied as a top layer for a second interference layer. This pigment has the disadvantage that white cannot be produced, since the metal particles absorb light and thus darken the product. In addition, the production is very expensive, since four different layers have to be applied using different methods. /6

A pigment with similar structure is known from EP-A-0 484 108. Titanium is deposited by sputtering onto a titanium dioxide-mica pigment as the base material. A part of the titanium reduces the titanium dioxide of the base material to suboxides, which act as light-absorbing areas on the pigment surface. The titanium particles that remain unaltered give the pigment a metallic gloss.

Apart from the high manufacturing costs, only dark pigments with low transparency can be produced by this method. In addition, interference colors cannot be produced.

The task of the invention is to make available lamellar interference pigments with high gloss and high covering power or high transparency that can be produced by means of a simple and economic method.

This task is solved in accordance with this invention by making available a lamellar pigment with high gloss and high covering power or high transparency consisting of a transparent, inorganic, lamellar matrix, which can contain an additional component, where the additional component is a soluble or insoluble dye, and to produce the gloss, the matrix is coated on at least one side with one or more thin, transparent or semitransparent reflecting layers of metal oxides or metals. /7

In addition, this task is solved in accordance with the invention by a method for producing the pigments in accordance with the invention that consist of a transparent, inorganic,

lamellar matrix, which can contain an additional component and which is coated with one or more thin, transparent or semitransparent reflecting layers of metal or metal oxides, where

- a precursor of the matrix material is applied as a thin film to an endless belt,
- the liquid film is solidified by drying,
- the matrix is developed from the precursor in the solidified film by a chemical reaction,
- the resulting layer is then separated from the carrier medium and washed, and
- the particles are optionally dried, annealed, ground and classified,

which is characterized by the fact that the film that solidifies during drying is then treated with an acid and the resulting film particles are coated with one or more reflecting layers of metal oxides or metals.

Expedient embodiments are given in the subordinate claims.

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In addition, an object of the invention is the use of the pigments produced in accordance with the invention in formulations like paints, printing inks, cosmetics or plastics, or as corrosion protection agents.

The pigments in accordance with the invention are based on a lamellar transparent matrix which can be modified by network-forming agents or network modifiers, such as aluminum oxide, boron oxide or phosphorus oxide, sodium oxide, lithium oxide, potassium oxide or calcium oxide. The matrix can consist, for example, of silicon dioxide, silicates, boron oxide, borates, aluminum oxide, aluminates, or other transparent, stable materials that are capable of absorbing soluble or insoluble dyes. The lamellar matrix particles typically have a thickness between 0.05 and 5 μm , and especially between 0.2 and 2.0 μm . The other two dimensions are typically between 1 and 250 μm , and especially between 2 and 100 μm .

Solutions of inorganic or organic compounds of the metals aluminum, silicon, potassium or sodium with, for example, borates, aluminates, poly- or metaphosphates, silicates or mixtures of these are used as the starting material (precursor) for producing the matrix. One preferred precursor is water glass.

Pigment particles whose measurements are clearly smaller than those of the matrix are laid in the matrix, generally spatially irregularly, as insoluble dyes. These are spherical or three-dimensionally irregularly shaped particles with a maximum dimension of less than 3 μm , and especially less than 1 μm , with even smaller particles being preferred in many cases. Agglomerates of commercially available pigments, which are too large, are preferably size-reduced in a ball mill, in a sand mill or a similar device. However, sometimes larger pigment particles can also be used, but the average size of the pigment particles in any case should be smaller than the average thickness of the matrix in order to allow the formation of smooth, thin, glossy layers. The term pigment particle here is to be understood broadly and includes white, black, colored and luminescent pigments.

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Suitable inorganic pigment particles are, for example, white pigments, like titanium dioxide, barium sulfate or zinc oxide, black pigments, such as magnetite or pigment carbon black, or colored pigments, such as iron or chromium oxide, mixed phase oxides like $(\text{Ti, Cr, Sb})\text{O}_2$, CoAl_2O_4 (Thenard's blue), ZnAl_2O_4 (Rinman's green), $(\text{Fe, Cr})_2\text{O}_3$, other sulfides such as CdS , and other inorganic colored pigments. Also suitable are inorganic fluorescent pigments, such as fluorescent silver-doped zinc oxide, phosphorescent copper-doped zinc sulfide, or ultramarine pigments.

Suitable organic pigments are azo pigments, anthroquinone pigments, indigo or thioindigo derivatives, diketopyrrolopyrrole pigments, perylene pigments, or phthalocyanine pigments.

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The pigment particles listed here are known, as are methods for producing them (for example, H. Kittel, Wissenschaftliche Verlagsgesellschaft, Stuttgart, 1960, G. Benzig, Pigments for paints [in German], Expert Verlag 1988), and as a rule, they are also commercially obtainable. However, these pigment particles are to be understood only as examples and they are intended only to illustrate the invention, without limiting it in any way. Besides the explicitly mentioned pigment particles, a large number of other pigment particles can be used.

In many cases, it is advantageous to add wetting agents for better dispersion of the pigment particles in the precursor solution, for example, commercially available nonionic and/or ionic types. For instance, polyethylene and polypropylene glycols are well suited. Neither the type nor the amount of the added wetting agent is critical, but in general, the amount of the wetting agent is a maximum of 2 wt% with respect to the dispersion.

The matrix can also contain a soluble dye as an additional component. The term "soluble dye" is understood to mean either a color-producing metal oxide or a soluble organic dye. These soluble dyes can be contained in the inorganic matrix either as the only component or together with an insoluble dye, i.e., a pigment. The soluble organic dye is, for example, a hydroxyanthraquinone dye that is soluble in sodium hydroxide solution or an acid azo dye.

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To prevent possible "bleeding" of the soluble dye from the matrix during the coating with the metal oxide, an SiO_2 layer can additionally be applied to the matrix.

The color-producing metal oxide is, for example; iron oxide, chromium oxide, or cobalt oxide. Generally speaking, colorant compounds of the metals titanium, vanadium, chromium, manganese, iron, cobalt, nickel, and copper, preferably compounds of cobalt, copper, iron and chromium, are suitable for coloring the matrix. They are added to the precursor of the matrix material as soluble compounds.

One obtains a colored transparent pigment with a color scale similar to that of colored transparent glass. For example, red-brown tones are obtained through the addition of iron

compounds, green tones through the addition of chromium compounds, and blue tones through the addition of cobalt compounds.

The pigment has particularly high transparency, since because of the smooth surface of the flakes and the lack of light-scattering particles in the matrix, practically no light becomes scattered.

The gloss of the matrix particles that already exists because of the smooth surface is enhanced through the application of reflecting layers, for example, of metal oxides. At the same time, interference colors are produced. /12

Through the combination of gloss effect and absorption color, brilliant color impressions can be realized, for example, for automobile paints or for dyeing plastics.

The colored matrix particles can also be used in various formulations without additional coating.

The soluble or insoluble dye is contained in the uncoated substrate in an amount from 0.01 wt% to 50 wt%, preferably 1 wt% to 30 wt%.

It was found that the addition of barium sulfate to the matrix produces a smoothing of the surface of the lamellar matrix particles. In this way, higher pigment gloss is achieved in the subsequent coating with metals or metal oxides.

Barium sulfate, with a particle size from 20 nm to 500 nm, preferably 100 nm to 300 nm, is dispersed in the precursor of the matrix material. This can be a commercially available product, for example, BF 10 from the Nordmann Company, Rassmann GmbH & Co.

The amount of barium sulfate in the uncoated substrate is 1 wt% to 50 wt%, preferably 10 wt% to 25 wt%. /13

The lamellar matrix particles, which contain an insoluble and/or soluble dye, are coated with one or more thin, transparent or semitransparent, reflecting layers of metal or metal oxides, which serve to produce a gloss.

Pigments whose matrix is coated on at least one side with a thin, semitransparent metal layer are preferred in accordance with the invention. The metal layer typically has a thickness between 5 and 25 nm and especially between 5 and 15 nm and consists, for example, of Al, Cr, Ag, Au, Cu, or even other metals. The metal layer is very smooth and reflects, mirror-like, a greater or lesser amount of incident light, in each case according to its thickness. The remaining light enters the matrix and, if there is an absorption pigment particle present, is partially absorbed and partially scattered at the incorporated pigment particles, and the remainder of the light is transmitted. If the pigments in accordance with the invention are applied to a surface, for example, as a component of a paint formulation, they arrange themselves more or less parallel to each other in overlying layers because of their lamellar structure, and the light passing through upper layers is, as just described, reflected at lower layers, absorbed, scattered and transmitted.

The overall effect produced by the particular arrangement of the pigments in accordance with the invention that was just described is a high gloss that is variable in a wide range in combination with the color of the incorporated pigment and high covering power, which is due to the reflection at the metal top layer and the scattering at the incorporated pigment particles. To enhance the gloss, the pigments can also be provided on both sides with a thin, semitransparent metal layer, which is particularly preferred. /14

In another particular embodiment of the pigments in accordance with the invention, the matrix provided with pigment particles is provided with a thin, smooth metal oxide layer, where the refractive index of the metal oxide layer is greater than the refractive index of the matrix material. Suitable metal oxides are, for example, titanium dioxide, zirconium dioxide, zinc dioxide, iron oxide, and/or other high refractive index metal oxides. The metal oxide layer, whose thickness is typically between 20 and 250 nm, acts as an interference or gloss layer and additionally possibly as an absorption layer, if the metal oxide is colored. The interference or gloss effect comes into existence through the fact that light at the interfaces of the ambient medium/metal oxide layer and the metal oxide layer/matrix surface is in part reflected mirror-like, and the reflected rays interfere with each other and, if the metal oxide layers are of appropriate thickness, produce interference colors. As with the matrix particles coated with a metal layer, this is a multiparticle effect, since the light reflected from different parallel aligned particles contributes to an enhancement of the interference color. The unreflected part of the light reenters the matrix, and there, as described, is partially transmitted and partially scattered. One obtains a glossy pigment with high covering power that has an interference color that is dependent on angle of viewing and the color of the incorporated absorption pigment particles that is not dependent on the viewing angle, and the latter can optionally be modified by the absorption color of the metal oxide layer. To enhance the effect, it is also possible for both sides of the pigment to be coated with a metal oxide layer, which is especially preferred. /15

Pigments with such a "color flop," viewing-angle-independent body color and viewing-angle-dependent interference color can be used, for example, in the printing industry for copier-protected originals.

If carbon black is incorporated into the matrix as an insoluble dye, the black background causes the matrix material coated, for example, with titanium dioxide to produce a pigment in which the body color [color of the non-self-luminous body] is the same as the interference color. A new kind of pigment is obtained in this way.

Coating the lamellar matrix particles that contain an insoluble and/or soluble dye takes place by known methods in accordance with DE 20 09 566, DE 23 13 331, DE 31 51 355 or DE 32 21 045.

Coating transparent matrix flakes with high-refractive-index metal oxides produces particularly transparent, highly glossy pigments.

Besides the two particular embodiments of the pigments in accordance with the invention that have been described, the invention also includes ones with more complicated structure. For instance, to achieve particular color effects or particular functional properties, the pigments can be covered with one or more other metal oxide layers. It may be mentioned as an example that to increase stability in enamels and glazes, the pigments can be provided with an additional top layer of tin or cerium dioxide, as described in DE 35 35 818. In addition, an additional metal oxide layer of, for example, tin oxide doped with antimony oxide (DE 38 42 330), or other electrically conductive top layers can give the pigments in accordance with the invention electrical conductivity. A particular optical effect can be achieved, for example, if an uncolored metal oxide layer is combined with a colored metal oxide layer, as proposed in US 3,087,828. Pigments in accordance with the invention with no more than 2 metal oxide layers are preferred. /16

To protect hydrolysis sensitive metal layers of Al, for example, it is possible to apply polymer protective layers of polyethylene, polyacrylates or other materials, for instance. In addition, metal layers can also be combined with metal oxide layers to produce particular effects; for instance, a metal/metal oxide/metal layer sequence on the matrix surface can act like a particularly effective interference layer, where the thickness of the metal oxide layer determines the optical path length difference between the rays reflected at the metal layers and thus, the interference color.

The thickness of the top layers can vary in a wide range. It is typically between 5 and 25 nm, while the thickness of metal oxide layers, as a rule, is between 20 and 300 nm. Polymer protective layers, as a rule, are not thicker than 50 nm. The ratio of the thickness of the matrix to the thickness of the layers applied to one side of the pigments in accordance with the invention is between 0.01 and 500 and especially between 0.1 and 150. /17

The covering power and, in the case of colored pigment particles, the viewing angle-independent absorption colors of the pigments in accordance with the invention can be varied in a wide range through the concentration of the incorporated pigment particles. The weight fraction of the incorporated pigment particles with respect to the weight of the uncoated substrate is typically between 0.5 and 40%, and especially between 5 and 25%. Particularly preferred are pigments in accordance with the invention with white or black pigments, where, in particular, titanium dioxide or carbon black particles, respectively, are used here.

The color of pigments that contain incorporated carbon black particles can, in each case according to the concentration of the carbon black particles, range from dirty white through light gray, metal-colored, dark gray, all the way up to black. Metal-colored and especially aluminum-colored pigments are particularly interesting. Since gloss is given to these pigments

through the subsequent coating with thin transparent metal oxide layers of, for example, titanium, zirconium, tin or zinc oxide, they can replace lamellar metal pigments, for example, in water-based paint formulations, where metal pigments and especially aluminum pigments can only be used with protective layers of organic polymers, for example, because of corrosion problems (formation of hydrogen). Moreover, there are often problems with corrosion-protected metal pigments, since the organic protective layer can become mechanically damaged ("scratched"). The glossy metal colored pigments in accordance with the invention that contain carbon black incorporated in a transparent matrix are extraordinarily stable both chemically and mechanically and they have high brilliance and high aesthetic appeal. For this reason, they are particularly suitable as substitutes for metallic pigments in various applications, especially for water-based formulations. /18

In addition, pigments in accordance with the invention with one or more organic or inorganic and especially inorganic pigments are preferred; carbon black, titanium dioxide, iron oxides, chromium oxides, cobalt oxide and colored spinels such as cobalt aluminum oxide are especially preferred.

A particularly high gloss as a rule is obtained when metal layers are used, but aesthetically impressive gloss effects can also be produced with metal oxide layers. The achievable gloss of the pigments in accordance with the invention can also be optimized in a wide range in regard to the particular application.

The overall aesthetic impression of the pigments in accordance with the invention can, if desired, be emphasized and rounded off by an interference effect, as described above. The pigments in accordance with the invention are thus optical systems with an excellent combination of optical properties, whose relative degree of expression can additionally be varied and optimized in a wide range with regard to a particular application. This optimization can be conducted as a matter of routine by a specialist on the basis of this description without any inventive activity being necessary. /19

The production of the pigments in accordance with the invention takes place in a continuous process using an endless conveyor belt, for example, in a continuous conveyor belt process or in a continuous drum process.

First, the conveyor belt method will be illustrated by means of the schematic drawing in Figure 1. The endless belt 1, which is passed over a roller system 2, goes through a feed section where it is coated with a thin film of the precursor. The application of the precursor together with the dye takes place by known methods, for example, via a roller system 3 or a nozzle 4. This nozzle can be designed as a single- or multicomponent nozzle. In addition, to adjust the layer thickness of the applied film, an adjustable orifice 5 or an air brush, in which a sharp jet of air is

blown through a slot nozzle, are provided. Coating the conveyor belt by doctor blade or by dip coating is also possible.

The combination of one-sided or two-sided dip coating of the conveyor belt followed by leveling of the applied layer using an air brush has proved to be particularly advantageous.

The dye is either dispersed or dissolved in the precursor before being applied to the conveyor belt, or the components are applied to the belt separately via several nozzles. The dispersion of the pigment particles in the precursor takes place by known methods, for example by means of an ultrasonic bath. Dispersion using a bead mill also proved to be particularly advantageous. /20

The coated conveyor belt is then passed through a drying zone, which can consist of one or more sections. One preferred embodiment of the drying zone consists of a predryer device 6, in which the film is provided with hot air at 80-150°C, and a subsequent IR drying device 7. In addition to these, however, other embodiments of the drying zone are also possible. The total heating power of the drying zone is, among other things, dependent on the speed of the conveyor belt and is between 0.5 and 10 kW per m of belt width. The belt speed is between 1 and 1000 m/min and in particular between 100 and 500 m/min, but large variations from these values are also possible. The specialist can easily match the heating power of the drying zone and the conveyor belt speed to each other.

The use of water glass as a precursor requires an acid bath 8, in which the alkali silicate film applied to the belt is converted to silicon dioxide. The alkali ions are then washed out of the matrix in a wash vessel 9.

The acid treatment takes place either by passing the belt through a container filled with acid or by exposing the applied film to hydrogen chloride gas. /21

The concentration of the acid is set to 1-20%, preferably 5-15%. The following can be used as acids: hydrochloric acid, phosphoric acid, sulfuric acid, nitric acid, titanium tetrachloride solution, iron chloride solution, tin chloride solution, as well as organic acids such as acetic acid.

The conditions in the acid bath must be chosen so that essentially only the alkali ions diffuse out, while the other cations that are added remain behind. Since alkali ions have very high coefficients of diffusion for diffusion from the SiO₂ matrix taking place in an acid, selective dissolving out of the alkali ions can generally take place by choosing the residence time of the film in the acid bath to be short or by using a weak acid such as phosphoric acid.

The layer that forms is then separated from the conveyor belt by a device. The separation can take place either mechanically by scraping or brushing or in a contactless method by detaching a "release layer" or by means of ultrasound. Separation with a liquid or gas jet 10 proved to be advantageous. Separation of the film in wet state has proved to be particularly

gentle to the material, since in this case, the material adheres less to the conveyor belt and the wet material scratches the conveyor belt less as it becomes detached.

If the matrix flakes are to be coated with metal oxide layers, a wet-chemical reaction layer is added to the conveyor belt method, in which the lamellar matrix material is suspended in water and coated with a smooth metal oxide or hydroxide top layer by adding one or more metal salt solutions at a pH value suitable for deposition of the relevant metal oxides or metal hydroxides. It is also possible for mixed oxide or hydroxide layers and even several top layers to be deposited in succession. This subsequent wet chemical reaction step is substantially known and is described in DE 19 59 988, DE 22 15 191, DE 22 44 298, DE 23 13 331, DE 25 22 572, DE 31 37 808, DE 31 37 809, DE 31 51 343, DE 31 51 355, DE 32 11 602 and DE 32 35 017.

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For better adhesion of the metal oxide layer to the matrix, it is expedient to first coat the matrix with a tin dioxide layer.

If pigments with a metal top layer are to be produced, the conveyor belt with the dried film is passed through a PVD zone.

However, coating with metals, for example silver, copper or gold, can also take place in a wet chemical process.

To ensure a continuous conveyor belt process, the belt in this case is preferably passed through successively connected vacuum chambers, which are differentially evacuated. The deposition of metal then takes place, as a rule, by evaporation, sputtering, or plasma polymerization in the innermost chamber, which has the highest vacuum.

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Continuous conveyor belt methods are known from US 3 138 475 or EP 0,240,952.

Other devices can also be used instead of the described arrangement. For example, a quasi-continuous process can be realized with an arrangement that follows the teaching of the device given in US 3,767,443, Figure II. Here a very long conveyor belt is wound onto a drum (of item 12 in Figure II from US 3,767,443); the belt is then unwound over a coating section, in which first a release layer and then the water glass film were applied, which are subsequently dried and optionally reacted with a mineral acid. Then the coated conveyor belt is wound onto a storage drum (item 15 in Figure II). After the conveyor belt has been completely wound up, the storage drum is put into a bath in which the release layer is dissolved, whereupon the dried matrix film separates from the conveyor belt. In general, the coated carrier film is not treated with a mineral acid before being wound onto the storage drum, since the resulting SiO_2 film can in some cases separate from the conveyor belt. After dissolving the release layer, matrix flakes are obtained, which are separated and treated with an acid.

The described drum arrangement can also be used for a quasi-continuous process. Thus, the conveyor belt is coated with the precursor in a first step and the precursor is then dried. After the belt coated with the dried matrix film has been completely wound onto the storage drum, the

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precursor holder is immersed into a mineral acid, so that the direction of travel of the belt changes and the supply and storage drums exchange roles. After passing through the acid bath and optionally a stripping device, the belt is free of the matrix film and a new cycle can begin. This modified drum process is a variant of the continuous belt process shown in Figure 1, and after has the advantage that the corresponding set-up can be more compact; the exchange of water glass and acid containers required after complete unwinding of the belt is a drawback.

The arrangements described here are to be understood as examples and are intended to illustrate the invention without limiting it. In general, continuous processes are preferred over quasi-continuous or even discontinuous processes.

It turned out that the use of conveyor belts that are made from thermally stable plastics is in many cases advantageous. The softening point of the plastic should not be lower than 150°C and, in particular, not lower than 180°C, in order to guarantee sufficiently high drying temperatures. In addition, the plastic materials should be largely chemically inert and, in particular, should not be attacked by dilute mineral acids. Suitable conveyor belt materials are, for example, polyethylene terephthalate, other polyesters, and polyacrylates, where this listing serves only for illustration and is not intended to limit the invention. /25

The plastic conveyor belts typically have a thickness of several tens of μm up to a few mm, where, in general, thicknesses between 0.1 and 2 mm are particularly preferred. However, in extreme cases, thicker plastic conveyor belts can also be used. The width and length of the plastic conveyor belts is generally less critical and can be optimized with regard to the relevant requirements.

Such plastic conveyor belts, as a rule, already have a smooth surface.

However, it is also possible to use thin metal belts of, for example, acid-resistant coated stainless steel or other metals that are inert with respect to dilute mineral acids, where the geometric measurements of these conveyor belts essentially correspond to those of plastic conveyor belts. The metal belts have high flexibility and stability and can be polished by traditional methods to improve surface quality.

Optionally, a release layer can first be applied to the conveyor belt used as the carrier medium in order to facilitate the separation of the matrix film; in quasi-continuous processes, the application of a release layer in some cases is unavoidable. /26

For example, a thin layer of a water-soluble polymer such as polyvinyl alcohol (PVA) that dissolves in the acid bath and in this way leads to complete separation of the matrix film can serve as the release layer. Silicone paints and substances such as hard waxes that become volatile or decompose without the formation of carbon black when heated are proposed in US 3 138 475 as materials for the release layer. The use of a release layer even in continuous processes has the advantage that in some cases a stripping device can be omitted.

The production of the pigments in accordance with the invention can also take place with the aid of a continuous drum process, which is illustrated below by means of the schematic drawing in Figure 2.

The devices for the individual process steps are arranged at certain segments at a rotating drum (1), as was already described for an endless belt. A precursor is applied as a thin film to the acid-resistant surface. The application preferably takes place via a roller system 2, but a spray device 3 can also be used. The drum then passes through a zone that is designed as a drying zone or reaction zone. The liquid film is solidified here either by irradiating it via a device 4 and/or mixing it with reagents, for example an acid, via a spray device 5. /27

The solidification of the film can take place by means of infrared radiation, by microwaves, by hot air, or by heating the drum from inside.

The resulting layer is separated from the drum surface by a separation device 6. The separation can take place with the aid of an air jet, a so-called air knife, by water jet or by a mechanical device. The resulting lamellar material is then processed further as already described.

Commercially available water glass is preferably used as the precursor for the preparation of the pigments in accordance with the invention; for instance a 35% Na water glass can be obtained from E. Merck, Darmstadt, under the name "sodium water glass, very high purity (item No. 5621)," where 35% is the % by weight with respect to the weight of the water glass.

Potassium or ammonium water glass or their mixtures can also be used. The commercially available water glass is preferably diluted with water, in each case according to its concentration, until a 5-25%, especially 10-20%, aqueous solution is present.

The properties of the water glass solution and the matrix can be modified by additions. For instance, an addition of Na aluminate solution (Si:Al ratio about 100:1) brings about a change of the matrix properties, which can lead to better processability. Particularly preferred additions are aluminate, borate and/or phosphate. /28

In addition, it is also possible to add other additives to the water glass solution, for example, surface-active substances or viscosity-increasing agents.

The thickness of the water glass film applied to the conveyor belt is, for a constant belt speed, optionally regulated via the variable orifice. The belt is kept very flat in the orifice region through appropriately arranged rollers, i.e., any "sagging" is avoided. The orifice edge is very precisely adjusted, with the distance between the lower edge of the orifice and the conveyor belt surface typically being between about 1 and 20 μm . The distance can typically be adjusted to a precision of about $\pm 1 \mu\text{m}$ or less. Since for a water glass concentration of about 15% the thickness of the SiO_2 particles obtained after annealing has decreased to about 1/10 of the thickness of the original water glass film, this means that the layer thickness tolerance for the SiO_2 particles is about $\pm 0.1 \mu\text{m}$; if the layer thickness of the SiO_2 particles is 0.5 μm or more,

this is 20% or less, which can be interpreted as sufficient in general. In the case of the layer thicknesses of about 1 μm or more that are quite common in practice, the layer thickness tolerance is 10% or less. If very thin flakes with a thickness of, for example, less than 0.5 μm are to be obtained with a layer thickness tolerance of about 10%, more highly diluted water glass solutions can be used in this case. /29

The layer thickness and the layer thickness tolerance of the substrates in accordance with the invention can be influenced in a targeted way through the choice of the concentration of the water glass solution and the drying conditions, and very thin particles with a layer thickness tolerance (= standard deviation of the layer thickness) of about 10% can also be obtained. Lamellar silicon substrates with a layer thickness distribution that is well defined in this way have not been described in the prior art and are also not accessible with the known production methods.

The lamellar pigments produced by the method in accordance with the invention are characterized by excellent surface quality and very uniform thickness. The standard deviation designated as thickness tolerance is no larger than 10%. A very high color uniformity and very high color strength are achieved through the planoparallel surface and the narrow thickness tolerance of the matrix flakes. With regard to their properties, i.e., their covering power, they can be tailor-made to the relevant application, since the covering power is dependent on the number of pigment particles in the matrix. The more pigment particles there are suspended in the matrix, the greater the covering power will be.

The color of pigments that contain incorporated carbon black particles can, in each case according to the concentration of the carbon black particles, range from dirty white through light gray, metal-colored, dark gray, all the way up to black. Metal-colored and especially aluminum-colored pigments are of particular interest. /30

The pigments produced by the method in accordance with the invention have a very broad spectrum of applications.

They can be used in formulations like paints, cosmetics or plastics. The pigments can have a high form factor (aspect ratio). For this reason, they can be added to paints or plastics as a diffusion barrier, for example, in particular as a corrosion protection agent (diffusion barrier for acids).

The complete disclosure of all of the applications, patents and publications listed above and below as well as the corresponding applications DE P 4134600 (October 18, 1991), DE P 4138376 (November 22, 1991), DE P 4212119 (April 10, 1992), DE P 4215276 (May 9, 1992), are contained in this application by reference.

The examples given below are intended to illustrate the invention without limiting it.

Example 1

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A continuous belt of polyethylene terephthalate (Melinex O; ICI; 12.5 cm wide; speed: 10 m/min) is coated with a water glass film about 10 μm thick by roller coating in the opposite direction (reverse roll coating). The water glass solution is made by diluting commercial water glass (sodium water glass, very high purity, E. Merck) with water in a 1:2.5 ratio, adding 0.2 wt% of a surfactant (Pricol extra, Henkel). The dilute water glass solution has a silicon dioxide content of 7.7%. The water glass film is dried in a drying section by supplying infrared radiation and hot air. Then the conveyor belt passes through an acid bath containing 10% hydrochloric acid and then a water bath. Upon leaving the water bath, the gel-like silicon dioxide film is separated by water jet and rinsed in a water bath. The broken lamellar pieces are filtered in a filter centrifuge and washed with demineralized water to a pH of 5-6. The filter cake is ground at stage 5 in an aqueous suspension in a laboratory mill (rotor GT 800, manufacturer: Rotor).

The resulting SiO_2 flakes have a diameter of 20-100 μm and an average thickness of 500 nm.

Example 2

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6 g wetting auxiliary (Pricol GV; Henkel) is dissolved in 2 L demineralized water. 1 L sodium water glass, very high purity (E. Merck) is stirred into this solution. 100 mL of an aluminate parent solution produced by dissolving 32 g sodium aluminate in 500 mL demineralized water is added to this solution.

The solution is processed on an endless belt as described in Example 1.

A lamellar SiO_2 matrix with aluminum as network-forming agent in a concentration of 1 atom% with respect to silicon is obtained.

Example 3

6 g wetting auxiliary (Pricol GV; Henkel) is dissolved in 2 L demineralized water. 1 L sodium water glass, very high purity (E. Merck) is stirred into this solution. 100 mL of a borate parent solution that is obtained by dissolving 21 g boric acid (E. Merck) in 300 mL demineralized water and adjusting the pH to a value of 12 with dilute sodium hydroxide is added to this solution.

The solution is processed on an endless belt as described in Example 1.

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A lamellar SiO_2 matrix with aluminum as network-forming agent in a concentration of 1 atom% with respect to silicon is obtained.

Example 4

6 g wetting auxiliary (Pricol GV; Henkel) is dissolved in 2 L demineralized water. 1 L sodium water glass, very high purity (E. Merck) is stirred into this solution. 100 mL of a phosphate parent solution that is prepared by dissolving 24 g $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ (E. Merck) in 300 mL demineralized water and adjusting the pH to a value of 12 with dilute sodium hydroxide is added to this solution.

The solution is processed on an endless belt as described in Example 1.

A lamellar SiO_2 matrix with aluminum as network-forming agent in a concentration of 1 atom% with respect to silicon is obtained.

Example 5

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100 g SiO_2 flakes are suspended in 1500 mL demineralized water. Then, with vigorous stirring at 75°C and at a pH of 1.8, a SnCl_4 solution (preparation: 11.5 g SnCl_4 is mixed with 38 mL concentrated hydrochloric acid and this solution is filled to 192 mL with demineralized water) is added by drops at a dispensing rate of 0.5 mL/min. Then, under the same conditions and at the same dispensing rate, a TiCl_4 solution (TiCl_4 content 375 g/L) is added by drops. The pH in each case is kept constant by adding 16% sodium hydroxide solution.

After the addition of about 110 mL, the product is filtered, washed until neutral with demineralized water, dried and annealed at 800°C for 30 min.

A highly transparent, silver-colored interference pigment with excellent gloss is obtained.

The coloristic data compared to a silver-colored interference pigment based on mica (Iriodin 130, E. Merck) are found in Table 1.

Example 6

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100 g SiO_2 flakes are suspended in 1500 mL demineralized water. Then, with vigorous stirring at 75°C and at a pH of 1.8, a SnCl_4 solution (preparation: 11.5 g SnCl_4 is mixed with 38 mL concentrated hydrochloric acid and this solution is filled to 192 mL with demineralized water) is added by drops at a dispensing rate of 0.5 mL/min. Then, under the same conditions and at the same dispensing rate, a TiCl_4 solution (TiCl_4 content 375 g/L) is added by drops. The pH in each case is kept constant by adding 16% sodium hydroxide solution.

After the addition of about 220 mL, the product is filtered, washed until neutral with demineralized water, dried and annealed at 800°C for 30 min.

A highly transparent, golden yellow interference pigment with excellent gloss is obtained.

The coloristic data compared to a golden yellow interference pigment based on mica (Iriodin 207, E. Merck) are found in Table 1.

Example 7

100 g SiO_2 flakes are suspended in 1500 mL demineralized water. Then, with vigorous stirring at 75°C and at a pH of 1.8, a SnCl_4 solution (preparation: 11.5 g SnCl_4 is mixed with 38 mL concentrated hydrochloric acid and this solution is filled to 192 mL with demineralized water) is added by drops at a dispensing rate of 0.5 mL/min. Then, under the same conditions and at the same dispensing rate, a TiCl_4 solution (TiCl_4 content 375 g/L) is added by drops. The pH in each case is kept constant by adding 16% sodium hydroxide solution.

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After the addition of about 570 mL, the product is filtered, washed until neutral with demineralized water, dried and annealed at 800°C for 30 min.

A highly transparent, red interference pigment with excellent gloss is obtained.

The coloristic data compared to a red interference pigment based on mica (Iriodin 215, E. Merck) are found in Table 1.

Example 8

100 g SiO_2 flakes are suspended in 1500 mL demineralized water. With vigorous stirring at 75°C and pH 4.0 an FeCl_3 solution (FeCl_3 content: 5.4%) is added by drops at a rate of 0.5 mL/min. The pH is kept constant by adding dilute sodium hydroxide solution.

After the addition of about 1200 mL, the product is filtered, washed until neutral with demineralized water, dried and annealed at 800°C for 30 min.

A luminous, bronze-colored effect pigment with excellent gloss and high brilliance is obtained.

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The coloristic data compared to a bronze colored effect pigment based on mica (Iriodin 530, E. Merck) are found in Table 1.

Example 9

100 g SiO_2 flakes are suspended in 1500 mL demineralized water. With vigorous stirring at 75°C and pH 4.0, an iron chloride solution (FeCl_3 content: 5.4%) is added at a rate of 0.5 mL/min. The pH is kept constant by adding dilute sodium hydroxide solution. If necessary, products that arise due to secondary hydrolysis are removed by sedimentation.

After the addition of about 1375 mL, the product is filtered, washed until neutral with demineralized water, dried and annealed at 800°C for 30 min.

A highly transparent red effect pigment with excellent gloss is obtained.

The coloristic data in a comparison with a wine red effect pigment based on mica (Iriodin 534, E. Merck) are found in Table 1.

Example 10

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0.2 wt% methylene blue (E. Merck) is added in addition to 0.2 wt% of a surfactant (Pricol extra, Henkel) to the water glass solution described in Example 1. The mixture is applied to an endless conveyor belt and processed as described in Example 1. The product obtained after grinding in a laboratory mill is dried for 60 min at 110°C.

Blue glossy SiO₂ flakes with high transparency are obtained.

Example 11

200 g of the blue SiO₂ flakes obtained in accordance with Example 7 are suspended in 2 L demineralized water. The suspension is heated to 60°C and adjusted to pH 9 with 2N sodium hydroxide. While stirring vigorously and maintaining the temperature constant, 250 mL sodium water glass solution is added at a rate of 1 mL/min. The sodium water glass solution is made by diluting 26 mL sodium water glass, very high purity (E. Merck) with 224 mL demineralized water. By controlled addition of dilute hydrochloric acid, the pH is kept at 9.

After coating with SiO₂, the product is directly further coated with a reflecting metal oxide interference layer by known methods, for example, by the method described in US 4 086 100, Example 1.

Example 12

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An aqueous solution of citric acid (E. Merck) and CrCl₃·6H₂O (E. Merck) is added to the water glass solution described in Example 1 in order to obtain a concentration of 7% citric acid and 3% CrCl₃·6H₂O in the water glass solution. In addition, 3% Texapon® (Henkel) is added as a wetting auxiliary agent. The mixture is applied to an endless belt and processed as described in Example 1. The product obtained after grinding in a laboratory mill is dried for 60 min at 110°C. Glossy olive green flakes with high transparency are obtained.

Example 13

An aqueous solution of sodium methylenediamine tetraacetate (E. Merck) and CoCl₂·6H₂O (E. Merck) is added to the water glass solution described in Example 1 to obtain a concentration of 8% sodium methylenediamine tetraacetate and 3% CrCl₂·6H₂O in the water glass solution. In addition, 3% Texapon® (Henkel) is added as auxiliary wetting agent. The mixture is applied to an endless conveyor belt and processed as described in Example 1. The product obtained after grinding in a laboratory mill is dried for 60 min at 110°C. Glossy, lilac colored flakes with high transparency are obtained.

Example 14

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An aqueous solution of tartaric acid (E. Merck) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (E. Merck) is added to the water glass solution described in Example 1 to obtain a concentration of 6% tartaric acid and 8% $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in the water glass solution. In addition, 3% Texapon® (Henkel) is added as auxiliary wetting agent. The mixture is applied to an endless conveyor belt and processed as described in Example 1. The product obtained after grinding in a laboratory mill is dried for 60 min at 110°C. Glossy, brownish yellow flakes with high transparency are obtained.

Example 15

500 mL of a 3% dispersion of titanium dioxide particles (R506; Sachtleben Chemie; average particle size: 440 nm) in a water glass solution (sodium water glass, very high purity, E. Merck, dilution ratio with water 1:2.5) is prepared in a bead mill (Dispermat CV, VMA-Getzmann). 0.5 wt% of a stabilizer (Hydropalat® 884, Henkel), with respect to titanium dioxide, is added for better dispersibility, and 1 wt% of auxiliary wetting agent (Hydropalat® 875, Henkel), with respect to the ready-to-use dispersion, is added for better wettability of the endless belt.

The dispersion is applied as a thin film to an endless conveyor belt as described in Example 1 and the band is passed through a drying stretch, where the film is dried by infrared radiation and hot air. Then the belt is passed through an acid bath and a water bath. Upon leaving the water bath, the gel-like film is detached from the conveyor belt by a water jet and rinsed in a water bath. The detached fragments of the film are processed further as in Example 1.

100 g of the flakes obtained from the laboratory mill are suspended in 2.5 L demineralized water and coated with titanium dioxide in rutile form by the method described in US 4 086 100, Example 1.

A white pigment with high coverage and a silver gloss is obtained.

Example 16

12.3 g DPP red (Ciba Geigy), particle size 50 nm,

1.2 g stabilizer W-22 (Krahn-Chemie),

50 g demineralized water, and

200 g zirconium beads (1-2.5 mm)

are ground for 90 min at 2000 rpm. Then the beads are screened out and the resulting suspension is mixed with 800 mL demineralized water and 300 mL sodium water glass (E. Merck). The mixture is processed on an endless belt as described in Example 1. The flakes obtained from the laboratory mill are dried for 1 h at 110°C. A glossy red pigment is obtained.

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Example 17

50 g of the flakes obtained in Example 16 are suspended in 1 L water. Then a SnCl_4 solution (preparation: 5.8 g $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ dissolved in 7 mL concentrated hydrochloric acid and 75 mL water) is dispensed at a rate of 0.6 mL/min under vigorous stirring at 75°C and pH 1.8. Then the temperature is raised to 90°C and the pH is reduced to 1.5. During the addition of a TiCl_4 solution (TiCl_4 content 380 g/L) at 0.6 mL/min, the pH is kept constant by the addition of dilute sodium hydroxide solution.

A silver-colored interference [dye] is obtained after the addition of about 100 mL TiCl_4 solution, a red dye after the addition of 195 mL, a blue dye after 275 mL and a green dye after 300 mL.

The products are filtered, washed and dried. The various interference dye pigments show the red pigment color of the substrate independent of viewing angle and the interference color via the TiO_2 cutting in dependence on viewing angle, i.e., a color flop effect.

Coloristic measurements for color flop pigment

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The measurements are the CIE- $L^*A^*B^*$ values for a 1.7% paint chart on a black background. The measurement geometry was: interference color 70° (illumination)/95° (measurement) [gloss], body color 45° (illumination)/90° (measurement).

//insert table, page 43//

Key:	1	Interference color
	2	Silver
	3	Red
	4	Blue
	5	Green
	6	Gloss
	7	According to body color

The resulting color locations are shown in Figure 3.

Example 18

82.2 g Derussol C (carbon black dispersion, w = 21%, Degussa) is mixed with 300 mL sodium water glass, very high purity (E. Merck) and 680 mL demineralized water. Then 2.1 g Pricol (Henkel) is dissolved in the suspension as an auxiliary wetting agent. The suspension is processed on an endless conveyor belt as described in Example 1. The flakes obtained from the laboratory mill are suspended in water and coated with titanium dioxide by the method described in US 4 086 100.

The coated flakes are annealed at 800°C under a protective gas and processed in a known way. Depending on the thickness of the TiO₂ interference layer, one obtains variously colored (silver, gold, red, blue, green) body color pigments. /44

Example 19

115.3 g iron oxide red (Bayer),
3.9 g stabilizer W-22 (Krahn-Chemie),
600 g demineralized water and
200 g zirconium beads (diameter 1-2.5 mm)

are ground for 1 h at 3000 rpm in a bead mill. After screening the beads the suspension is mixed with 2250 mL demineralized water and 1140 mL sodium water glass, very high purity (E. Merck).

The suspension is processed on an endless belt as described in Example 1, the red flakes obtained from the laboratory mill are suspended in water and coated with metal oxides by known methods, for example, the method described in US 4 086 100, for interference colors.

Example 20

115.3 g iron oxide yellow (Bayer),
3.9 g stabilizer W-22 (Krahn-Chemie),
600 g demineralized water and
200 g zirconium beads (diameter 1-2.5 mm)

are ground for 1 h at 3000 rpm in a bead mill. After screening out the beads, the suspension is mixed with 2250 mL demineralized water and 1140 mL sodium water glass, very high purity (E. Merck).

The suspension is processed on an endless belt as described in Example 1. The yellow flakes obtained from the laboratory mill are suspended in water and coated for interference

colors with metal oxides by known methods, for example, the method described in US 4 086 100.

Example 21

115.3 g iron oxide black (Croda),
3.9 g stabilizer W-22 (Krahn-Chemie),
600 g demineralized water and
200 g zirconium beads (diameter 1-2.5 mm)

are ground for 1 h at 3000 rpm in a bead mill. After screening out the beads, the suspension is mixed with 2250 mL demineralized water and 1140 mL sodium water glass, very high purity (E. Merck).

The suspension is processed on an endless belt as described in Example 1. The black platelets obtained from the laboratory mill are suspended in water and coated for interference colors with metal oxides by known methods, for example, the method described in US 4 086 100. /46

Example 22

115.3 g chromium oxide (Croda)
3.9 g stabilizer W-22 (Krahn-Chemie),
600 g demineralized water and
200 g zirconium beads (diameter 1-2.5 mm)

are ground for 1 h at 3000 rpm in a bead mill. After screening out the beads, the suspension is mixed with 2250 mL demineralized water and 1140 mL sodium water glass, very high purity (E. Merck).

The suspension is processed on an endless belt as described in Example 1. The green platelets obtained from the laboratory mill are suspended in water and coated for interference colors with metal oxides by known methods, for example, the method described in US 4 086 100.

Example 23

115.3 g Berlin blue (Croda),
3.9 g stabilizer W-22 (Krahn-Chemie),
600 g demineralized water and
200 g zirconium beads (diameter 1-2.5 mm)

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are ground for 1 h at 3000 rpm in a bead mill. After screening out the beads, the suspension is mixed with 2250 mL demineralized water and 1140 mL sodium water glass, very high purity (E. Merck).

The suspension is processed on an endless belt as described in Example 1. The blue flakes obtained from the laboratory mill are suspended in water and coated for interference colors with metal oxides by known methods, for example, the method described in US 4 086 100.

Example 24

100 g of the SiO_2 flakes obtained as in Example 1 are dispersed in a mixture of
1000 mL 3% silver nitrate solution,
25 mL 40% formalin solution, and
25 mL methanol.

The suspension is slowly stirred overnight until all of the silver has precipitated from the solution onto the SiO_2 flakes. /48

The resulting silver-gray flakes are washed, dried and annealed at 800°C.
A silver-gray pigment is obtained.

[Key to previous page:]

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- | | |
|---|------------------|
| A | Table 1 |
| 1 | Glancing angle |
| 2 | Relative gloss |
| 3 | Covering power |
| 4 | (Example ____) |
| 5 | Black background |
| 6 | White background |

Claims

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1. A lamellar pigment with high gloss and high covering power or high transparency consisting of a transparent, inorganic, lamellar matrix, which can contain an additional component, which is characterized by the fact that the additional component is a soluble or insoluble dye and that, to achieve gloss, the matrix is coated on at least one side with one or more thin, transparent or semitransparent reflecting layers of metal oxides or metals.

2. A pigment as in Claim 1, which is characterized by the fact that the transparent inorganic matrix consists of silicon dioxide, silicate, boron oxide, borate, aluminum oxide, aluminate, or mixtures of these.

3. A pigment as in Claims 1 and 2, which is characterized by the fact that the inorganic matrix is modified with network-forming agents or network modifiers.

4. A pigment as in Claims 1-3, which is characterized by the fact that the inorganic matrix contains barium sulfate to smooth the surface.

5. A pigment as in Claim 4, which is characterized by the fact that the barium sulfate is contained in the uncoated substrate in an amount from 1 wt% to 50 wt%, preferably 10 wt% to 25 wt%.

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6. A pigment as in Claims 1-5, which is characterized by the fact that the insoluble dye is an organic or inorganic pigment.

7. A pigment as in Claim 6, which is characterized by the fact that the organic pigment is an azo pigment, an anthraquinone pigment, an indigo or thioindigo derivative, a diketopyrrolopyrrole pigment, a perylene pigment or a phthalocyanine pigment.

8. A pigment as in Claim 6, which is characterized by the fact that the inorganic pigment is carbon black, titanium dioxide, iron oxide, chromium dioxide, cobalt oxide or a mixed oxide.

9. A pigment as in Claims 1-5, which is characterized by the fact that the soluble dye is a soluble metal compound that leads to a color-producing metal oxide, or a soluble organic pigment.

10. A pigment as in Claim 9, which is characterized by the fact that the color-producing metal oxide is iron oxide, chromium oxide or cobalt oxide.

11. A pigment as in Claim 9, which is characterized by the fact that the soluble organic pigment is a hydroxyanthraquinone dye that is soluble in sodium hydroxide solution or an acid azo dye.

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12. A pigment as in Claims 1-11, which is characterized by the fact that the metal layer formed as reflecting layer consists of silver, gold, palladium, platinum, aluminum, chromium or copper.

13. A pigment as in Claims 1-11, which is characterized by the fact that the metal oxide layer formed as reflecting layer consists of chromium oxide, titanium dioxide, iron oxide, or a mixture of these, and serves to produce interference colors.

14. A pigment as in Claims 1-5 and 9-11, which is characterized by the fact that it consists of the lamellar matrix and a dye.

15. A pigment as in Claims 1-14, which is characterized by the fact that additional layers for particular physical and/or chemical requirements are applied to the reflecting layer or the matrix.

16. A method for producing a lamellar pigment with high gloss and high covering power or high transparency consisting of a transparent, inorganic, lamellar matrix that can contain an additional component and that is coated with one or more thin, transparent or semi-transparent reflecting layers of metal oxides or metals, where

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- a precursor of the matrix material is applied as a thin film to an endless conveyor belt,
- the liquid film is solidified by drying,
- the matrix is developed from the precursor in the solidified film by a chemical reaction,
- the resulting layer is then separated from the carrier medium and washed, and
- the particles are optionally dried, annealed, ground and classified,

which is characterized by the fact that the film that solidifies during drying, is then treated with an acid, and the resulting film particles are coated with one or more reflecting layers of metal oxides of metals.

17. A method as in Claim 16, which is characterized by the fact that solutions of inorganic or organic compounds of the metals aluminum, silicon, potassium or sodium with borates, chlorides, aluminates, poly- or metaphosphates, silicates, or mixtures of these are used as precursor.

18. A method as in Claims 16 to 17, which is characterized by the fact that the precursor is water glass.

19. A method as in Claims 16-18, which is characterized by the fact that network-forming agents or network modifiers in the form of soluble salts are added to the precursor.

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20. A method as in Claims 16-19, which is characterized by the fact that barium sulfate is added to the precursor to smooth the surface of the matrix.

21. A method as in Claims 16-20, which is characterized by the fact that fine particles of an organic or inorganic pigment are dispersed in the precursor before application to the endless belt or upon application to it.

22. A method as in Claim 21, which is characterized by the fact that the dispersed amount of pigment particles is 0.01-99 wt%, preferably 1-30 wt%, with respect to the precursor.

23. A method as in Claim 22, which is characterized by the fact that the dispersion of the pigment particles and the precursor is prepared in a bead mill.

24. A method as in Claims 16-23, which is characterized by the fact that the precursor is applied to the endless belt together with the aqueous solution of a metal compound and/or a soluble organic pigment.

25. A method as in Claim 24, which is characterized by the fact that the metal compound is masked by a complexing agent.

26. A method as in Claim 25, which is characterized by the fact that the complexing agent is citric acid, tartaric acid or EDTA. /55

27. A method as in Claims 24-26, which is characterized by the fact that the amount of the metal compounds in the precursor is 0.01-50 wt%, preferably 2-10 wt%.

28. The use of the pigments as in Claims 1-15 in formulations like paints, printing inks, cosmetics or plastics, or as agents to protect against corrosion.

//insert Figures 1-3, three pages//

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